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Separation of germanium, lead, zinc, and cadmium by anion exchange

Franklin Maynard Hill

SEPARATION OF GERMANIUM, LEAD, ZINC, AND CADMIUM BY ANION EXCHANGE

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FRANKLIN MAYNARD HILL

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F. M. H.

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INTRODUCTION

The object of this study was to investigate the ion exchange behavior of germanium and apply the anion exchange technique for the separation of germanium, cadmium, lead, and zinc.

A new interest in germanium has developed because of its recent industrial application as a semi-conductor.[6] Analytical methods for the separation and analysis of germanium in low concentrations have not been perfected. Krause and Johnson, in a recent review,[46] discussed and evaluated a number of methods.

Most of the methods for the analysis of germanium require a preliminary separation. The analytical methods for germanium reported in the literature are troublesome and time consuming. Therefore, it was considered worthwhile to investigate any separation method which offered possibilities of time or work saving.

Separation Methods

Distillation: Telford and Furman[68] are of the opinion that the best procedure for separation of germanium, from complex mixtures, is by distillation of the tetrachloride from a hydrochloric acid solution, according to the method of Johnson and Dennis.[33] Other analysts also recommend this procedure.[28]

Some earlier adaptations of the distillation of $GeCl_4$

as a method of separation, made no attempt to remove arsenic, thus allowing it to distil over with the germanium as the trichloride. Johnson and Dennis, modified the method of Buchanan[13] by passing chlorine gas through the solution during distillation. This converts the arsenic to As(V), thereby preventing it from distilling over with germanium. Most procedures are some adaptation of the Buchanan-Johnson-Dennis separation, whereas some use other oxidizing agents along with the chlorine. An excess of chlorine is desirable. Buchanan[13] used chlorine in his procedure as far back as 1916 as a preliminary separation method to confirm the presence of germanium in Missouri sulfide zinc ores. Browning and Scott[11] successfully substituted potassium permanganate, manganese dioxide, or potassium chlorate, for chlorine, in an adaptation of the Buchanan procedure for qualitative work. In a later report[12] they showed that potassium dichromate can also be used to keep the arsenic oxidized to As(V). For quantitative work, all methods require the presence of a large excess of chlorine to retain the arsenic as As(V).

Precipitation: Germanium can be precipitated by hydrogen sulfide in acid solution along with the arsenic group of sulfides. Separation from the copper group can be obtained by digestion with ammonium polysulfide. Germanium resembles tin in hydrofluoric acid solution, forming an anion as a fluo-compound. It can be separated from As(III) which precipitates on the addition of H_2S,[28] under these conditions.

Whereas arsenic will precipitate as the sulfide from dilute hydrochloric acid solution, a much more concentrated

acid solution is required for precipitation of the germanium disulfide. This latter property led to its discovery by Winkler.[70]

The use of tannin or quinine tannate as a precipitating agent for germanium was proposed by Davies and Morgan.[19] By varying the conditions, separations from many other metals can be obtained.

Germanium forms a precipitate with several organic reagents. A few of these compounds can be used in its estimation but so far none have been used in a general separation method.

Extraction: Schneider and Sandell[61] refer to Vanossi's use of the extractability of germanium from strong hydrochloric acid solutions by carbon tetrachloride. Sandell[60][61] and others have adapted the extraction method to analytical separations. The chief disadvantage is the fact that arsenic (III) is extracted along with the germanium (IV). The arsenic would have to be present in the (V) state in order to prevent this. Since this can be most readily assured by the passage of chlorine through the solution, an operation which is used in distillation separations, it is doubtful if carbon tetrachloride extraction offers many advantages over distillation. Schneider and Sandell[61] report excellent results for trace separations of germanium where they are not concerned with the presence of arsenic (III).

The distillation technique is probably the most generally applicable of the separation methods reported. They

all have disadvantages, especially for routine analyses. Therefore, separation of germanium by ion exchange seemed to be a worthwhile investigation. It was believed that any data collected would be of value, since very little has been published on the ion exchange behavior of germanium.[22]

REVIEW OF THE LITERATURE

Ion Exchange Resins

Ion exchange resins because of their nature, fall into four general classifications. They are: (1) strong acid, (2) weak acid, (3) strong base, (4) weak base.

The strong and weak acid types are cation exchange resins. This investigation involves the use of strong base or anion exchange resins, in analytical separations.

Anion Exchange Resins: The basic patents on organic ion exchange resins were taken out in 1936 by Adams and Holmes.[1] These earlier resins were condensation products of poly-phenols and aromatic polyamines with formaldehyde. They had very limited applications.

D'alelio,[18] in 1945, made perhaps the most outstanding contribution to the production of ion exchange resins. He developed a process for the manufacture of ion exchangers based on the idea of building up an inert three dimensional cross-linked hydrocarbon network structure by the co-polymerization of styrene with divinyl-benzene.

The introduction of sulfonic acid groups results in the formation of a strong acid type of resin.[4] In order to produce a strong base type exchanger a two step process is used. Methylene chloride groups are first introduced by treatment of the polymer with chloromethylether, followed by treatment with a tertiary amine. Dowex I used in this work is this type resin.

Although weak acid and weak base type resins find some application, the strong base resins are much more versatile. Under proper conditions a strong base anion exchange resin, such as Dowex 1, can exchange over the entire pH range. It is stable toward nearly all chemicals including most oxidizing agents.

Anion Exchange Theory

Anion exchange, by use of strong base type resins has not been as thoroughly examined as cation exchange. Generally speaking however, the theory of cation exchange, with some modifications, is applicable.(59)

Any organic anion exchange resin may be considered to be a cross-linked three dimensional structure, containing structurally bound ionogenic groups. The number of these ionized groups determines its exchange capacity. Unfortunately Dowex 1, and the other strong basic type resins do not have the high capacity of the sulfonic acid cation exchangers. Capacities of the strong basic type average 2.3-2.5 milleq. per gram of dry chloride form of resin.(49)

The affinity of an ion exchange resin is closely related to the degree of hydration of the ions which it adsorbs. When ions are very large as compared to the intermolecular resin space, steric effects will also enter into the degree of affinity.

With ions of differing valence, the ion with the higher valence will be more strongly attracted than the one of

lower valence. This phenomenon is more evident when dealing with cation exchange because of the greater counter influence of steric and anomolous hydration effects of complex anions. These effects are not as likely to be exhibited by simple cations. The more dilute the solution the greater is the affinity of the resin for the anion of higher valence.

Although the exchange potential series for weak anion exchange resins is not as sharp and clear cut as the lyotropic series for cations, Kunin and Myers[48] have shown that the following order prevails: hydroxide sulfate chromate tartrate nitrate arsenate phosphate molybdate acetate = iodide = bromide chloride fluoride. The effect of pH has a greater influence on the order than with the cation exchange series. In later work[49] they found that the same order prevails with strong base resins except the hydroxide ion is the weakest replacing ion instead of the strongest.

It is doubtful if this series could be specifically applied when working out separation technique in ion exchange chromatography. Generally however, it is useful. In this investigation the resin was always changed to the chloride form before adsorption of other ions onto the column. The above series indicates that the chloride ion should be one of the most easily replaced ions.

The effect of degree of cross-linkage on affinity, and separation of anions cannot be overstressed. The larger the percentage of cross-linkage, the smaller will be the anion

necessary to penetrate between those cross-links. More anions will be excluded and the influence of the smallness of anion size will have a greater effect on the exchange potential.

Anion Exchange Equilibria: Material written on ion exchange equilibria has been extensive and varied but practically all of it has dealt with cation exchange. It is believed however, that anion exchange processes behave similarly in many cases. Most of the material can be grouped under four headings:

1. Mass Action Relationships
2. Donnan Equilibria
3. Adsorption Relationships
4. Crystal Lattice Theory

The Crystal Lattice Theory of Pauling and Bragg, although very popular in explaining the ion exchange processes of the earlier inorganic exchangers, has not been extensively applied to organic exchange processes.

The reversibility of the ion exchange process, as well as the equivalence of it, led to the applicability of the Law of Mass Action in many forms. Many of the equations are essentially the same for ions of equal valence, but considerable variation results when dealing with equations of ions of mixed valence. Studies with organic resins, however, present evidence that Mass Action Law applications are only valid for exchange between two closely similar univalent ions.

Boyd and coworkers[10][8][9] have contributed much to the theory of ion exchange based on the Law of Mass Action. Boyd

believes that some of the difficulties involved are due to: (1) use of stoichiometrically incorrect equations because of hydrolysis, etc., and (2) the resin being assumed to contain only one active chemical grouping.

Gregor[58] and others have treated mass action in ion exchange from a thermodynamic standpoint. The problem of knowing what activities to use when dealing with internal resin solutions is particularly difficult to resolve.

Many studies on ion exchange have been made by use of a Donnan Equilibrium approach. Samuelson[59] summarizes the widely applicable Donnan Theory as applied to a sulfonic acid resin involving exchange of ions of equal valence. Experience has shown that the Donnan Theory is applicable to divalent or trivalent ion exchange only when due consideration of individual activities is made.

A comparison of the Donnan concept as applied to ion exchange with its original application to membranes draws the following analogies:

(1) The colloidal micelle to which is attached the exchangeable ion is considered to be the non diffusible ion.

(2) The interface between the solid and liquid phases is analogous to a membrane.

(3) In many simple ionic solids the Donnan concept cannot be applied, in which case all ions may diffuse. However, in organic resins there is always a high polymeric non diffusible ion.

Bauman and Eichorn[4] have made a simple study of the Donnan Equilibrium using Dowex 50 resin. H. P. Gregor[27] draws an instructive analogy between ion exchange processes based on the Donnan concept and a spring under tension. Osmotic pressure effects must always be considered. However, the Donnan treatment does not produce mathematical quantitative results at very dilute concentrations.

Several investigators have successfully applied the Freundlich isotherm to ion exchange processes. According to Kunin and Myers,[49] Wiegner and Jenny, and Vageler, among others used modifications of it.

Boyd, Schubert and Adamson[10] adapt a complicated form of the Langmuir equation to ion exchange processes. The application of Jenny's equation is summarized by Kunin and Myers.[49]

In their study of the anion exchanger Amberlite IR4B, Kunin and Myers[48] made one of the few experimental contributions to the study of anion exchange theory.

Glueckauf[24][25][26] has perhaps treated ion exchange more from a theoretical standpoint than any other person. His mathematical applications of both the Langmuir and Freundlich isotherms are useful relationships.

Practice of Column Technique

Of the two general techniques of ion exchange practice, batch and column, the latter has by far the largest number of applications. In chromatographic separations where a series

of equilibria is necessary, the packed column is used almost exclusively.

Samuelson[59] devotes several pages to the theory and practice of column operation. In general, we used the technique as summarized by him but sometimes found it advisable to make adaptations which could be applied to our specific problem.

Essentially ion exchange by column operation consists of:

(1) Adsorbing an ion, in solution, onto a column.

(2) Removing that ion from the column.

When chromatographic separation is desired, complications arise because of the necessity of progressively removing several ions without contamination by other ions. Adsorbing ions onto the column is known as sorption; and their removal, as elution. Sometimes an ion is not adsorbed by the resin, in which case it goes through in the sorption step.

In order to get metallic ions to adsorb onto Dowex 1 they have to be converted to the anion form. This we were able to do by use of 8-9N hydrochloric acid solution. Germanium, zinc, and cadmuim under controlled conditions will adsorb onto a strong anion exchange column, and lead will pass on through.

In dealing with ion exchange resins for analytical separations the concept of break through is very important. By definition, the break through point of a resin column is that point at which the ion being adsorbed can first be detected in the effluent by what ever analysis method is used. The

break through capacity is described in terms of material adsorbed at the break through point. The total capacity of a column is usually considerably greater than the break through capacity. This data is often plotted as a break through curve as illustrated by Samuelson.(59)

Probably the most widely accepted theory of break through curves is that of derived continuous variables as applied by Samuelson. Basically it states that the shape of break through curves is dependent upon the type of exchange isotherm governing the static equilibria.

There are several controllable factors which influence the break through capacity of a column.

(1) A decrease in particle size will cause it to increase.

(2) The break through capacity is almost a straight line function of the column length, since the amount of resin a column holds is also a function of its length.

(3) The break through capacity is also greater and the curve sharper when the volume of the resin is constant but the column longer.

(4) Kunin and Barry,(47) as well as Samuelson, have shown that the break through capacity is greater the lower the flow rate.

(5) Ketelle and Boyd(35) demonstrated that an increase in temperature increases the break through capacity.

(6) The acidity and composition of the solutions are

other variable factors which are used as more specific influences by which chromatographic separations may be improved.

Most of these conclusions were drawn from experiments based on the use of cation exchange resins in column operation, although Sussman, Nachod and Wood[67] have shown that the shapes of the curves for anion exchange resins, in principle, are the same as for cation exchange resins.

Some Previous Separations by Anion Exchange

Because of its stability and because of the excellent work which has been done with it, we decided to use Dowex 1 in our experiments. The availability of Dowex 1 with varying degrees of cross-linkage offers another tool for separation by the exclusion of certain large ions. Wheaton and Bauman[71] state that there is very little indication of capacity drop in its continued operation. Although they don't show the volume change for Dowex 1 in various ionic forms, we found it small and of little consequence. However, due to swelling, the maximum flow rate attainable in the chloride form of the 50-100 mesh resin is considerably less than in the hydroxide form. Wheaton and Bauman also give some valuable information on the selectivity of Dowex 1 for monovalent anions using the $Cl^{(-)}$ ion as standard. It was, however, of little practical value in our work since we were concerned with complex anions containing the metals.

The difference in selectivity of Dowex 1 for various anions of the same charge depends on the hydrated anion

radius. This radius does not necessarily follow the order of molecular weight. For example, it is more difficult for highly cross-linked Dowex 1 to take up the fluoride anion than the chloride anion because of the larger hydrated radius of the fluoride ion. Polyvalent anions greatly alter this concept as a basis for prediction since the uptake is greater the greater the negativity of the anion involved. The equilibrium constants for di- or tri-valent anions is also dependent on solution strength. Equilibrium curves, however, offer some basis for predicting operating conditions.

Per cent cross-linkage has a big effect on equilibrium values. These values approach the Law of Mass Action values near zero cross-linkage where the condition of a true solution exists. Although a highly cross-linked resin may admit anions with large hydrated radii, it cannot accomodate the total ionic content that a lower cross-linked resin can.

Simple anions were not considered in this investigation. Germanium, lead, zinc, and cadmuim must be converted to complex ions for separation by anion exchange. The work which has been done in this field is limited. Kraus and associates have been the most prolific workers with anion exchange. Huffman and others have also made contributions. The majority of the published material dates from 1949. Most of the experimental work was done using micro columns and radioactive counter technique. The adaptation of these micro separations to semi-micro methods was a factor we had to consider. Different analytical methods also had to be used.

The use of fluoride complexes of zirconium and hafnium for the separation of these elements by anion exchange was reported in 1949.[37] Kraus and Moore achieved partial separation with 200-300 mesh Dowex 1. They eluted with a solution consisting of 0.5M hydrofluoric acid and 1.0M hydrochloric acid. Micro quantities were involved and counter analysis technique was applied. Huffman and Lilly used Amberlite IRA 400 resin and a weaker hydrochloric acid - hydrofluoric acid elution mixture.

Kraus and Moore[38] obtained excellent separations of columbium and tantalum under conditions similar to their experiments with zirconium and hafnium. They postulate the formation of fluoride complexes with a charge of -2 or greater. A poor explanation of the difference in elution behavior is offered since in some complexes columbium and tantalum show practically the same ion size.

The anion exchange of zirconium, hafnium, niobium, and tantalum in HCl solutions was studied by Huffman, Iddings and Lilly.[30] Tantalum was not successfully separated from niobium but zirconium was separated from hafnium. No zirconium or hafnium appeared in the niobium-tantalum fraction.

Earlier the same year Kraus and Moore[41] reported favorable results using HCl-HF mixtures to separate zirconium and niobium. They also found that tantalum would adsorb under a variety of conditions.

Huffman and Oswalt[31] used Dowex 1, an anion exchange resin, to separate promethium and europium in trace quantities. Dowex 1 was also used by Kraus and Moore[39] in their

study of protactinium in hydrochloric acid solutions. It was successfully adsorbed from 8N acid and eluted with 4N or weaker acid. In this respect germanium was found to be similar.

In another report[43] Kraus and Moore showed that protactinium and iron can be separated by using HCl-HF for sorption and elution.

Kraus and Moore[40] applied the concept of elution constant to the study of adsorption and elution of iron in hydrochloric acid solution. They believe $FeCl_4^{(-)}$ forms in strong hydrochloric acid solution since the rate of elution decreases rapidly from 1M→9M acid strength, reaching a minimum at 9M. The elution constant approach isanother valuable method of making anion exchange studies. The elution constant is given by the equation: $E = dA/V$, where d is distance in cms. an adsorption band travels when V (ml.) of solution has been passed through a column of A (cm^2) cross sectional area.

In other studies Moore and Kraus[53] used the elution constant method on cobalt and nickel in hydrochloric acid solution. They found some surprising differences in their behavior considering their chemical similarity in most respects. Cobalt showed a maximum adsorption in 9M HCl but the adsorption of nickel was negligible in the entire range tested, which was 0.5-12M hydrochloric acid. Theoretical analogies of the complex forming properties of cobalt, nickel and iron (III) are given in which they say:

"(1) Non adsorbability of nickel (II) suggests that a negative complex is not formed.

(2) The greater adsorption of iron (III) with an increase in acid concentration and absence of a maximum is characteristic of singly negatively charged complex ions.

(3) Since cobalt is not strongly adsorbed in concentrated hydrochloric acid, $CoCl_4^{(=)}$ is probably present at this acid concentration. Doubly or more highly charged negative complexes possess this characteristic."

Kraus and Nelson[44] elaborate on this idea of adsorption in various acid concentrations versus complex ion formed. They postulate that $AuCl_4^{(-)}$ exists both in relatively weak acid solutions and concentrated acid solutions. They also explain the relation between ether extraction, complex formation, and anion exchange.

A study of the reports by Kraus and coworkers[42][45][54] prompted us to make a study of the separation of germanium from lead, cadmium, and zinc. In most of their work, Dowex 1, 200-230 mesh was used. They showed that the anion exchange behavior, and thus the complexing behavior of the transition elements, vary widely. An irregularity in degree of complexing versus atomic number is demonstrated. The order of complexing of divalent chlorides on the basis of anion exchange was found to be:

$$Zn > Cu > Co > Fe > Ni$$

This order is the same whether taken in the order in which

increased acid concentration will cause some adsorption, or whether taken in the order of maximum adsorption with increasing acid concentration. The first is thought to be related to the formation of $MCl_3^{(-)}$ to any extent whatsoever. The second method probably gives concentrations at which $MCl_4^{(=)}$ is formed. Kraus shows that although zinc is strongly adsorbed from any strong hydrochloric acid solution, 0.005M hydrochloric acid is recommended for elution.

The study[54] on lead in hydrochloric acid solution showed that the adsorption of Pb (II) is negligible in dilute hydrochloric acid solution. It reaches a maximum in 1.5M acid, and is again negligible above 8M acid concentration. The postulation was made that when the degree of adsorption increases with increasing acid concentration the positively charged species are dominant. When the degree of adsorption decreases with increasing acid strength the fraction of the metal in the form of negatively charged complexes is close to unity. The adsorption maximum would then be at those hydrochloric acid concentrations where negatively charged species become dominant. The existence of $PbCl_3^{(-)}$ or $PbCl_4^{(=)}$ has been suggested.

Cadmium was found to elute from a Dowex 1 column[51] using 10^{-4}M hydrochloric acid. Its complex forming properties were shown to be greater than zinc, since a weaker elution acid is required.

Jentzsch and Frotscher[32] tabulate the strength of hydrochloric acid required to elute eighteen different elements from Wofatit L 150. Germanium is not included. A

glance at the table will indicate the approximate conditions necessary to separate many of them. Although in general their results are similar to those of Kraus and associates, the elution acid strength required for Dowex 1 is not the same. The data reported by Jentzsch and Frotscher illustrates the relative degree to which a metal will form a complex anion in hydrochloric acid solution. They also tabulate the chloro complexes of many of the metals including lead, cadmium, and zinc.

The Formation of Complex Ions of Germanium, Lead, Zinc, and Cadmium

Germanium: The chemistry of germanium, expecially with respect to complex ion formation has not been thoroughly investigated. However, a few reports indicate that germanium forms complex ions under specific conditions.

Mattock[52] states the difficulties of dealing with germanium in solution when he says that the complicating effects of hydrolysis restricts quantitative interpretation. He used strong hydrochloric acid solution to lower these effects. Mattock assumes the presence of $GeCl_6^{(--)}$ or $GeCl_{6X}(OH)_X^{(--)}$ under these conditions. He also mentions the possibility of a higher germanium complex.

Pauling[56] has shown that it is possible to predict the type of aggregate two ions will form by considering the ratio of their ionic radii. He stated that 0.41 is the minimum ratio which will allow hexacoordination. On this basis Ge should form hexahalogen complexes with $F^{(-)}$ and $Cl^{(-)}$ but

only tetra compounds with $Br^{(-)}$ or $I^{(-)}$. Since the ratio in the case of germanium with chlorine is 0.42, very close to the limit, it is likely that the hexachloro-germanate will not form except under very favorable conditions.

Laubengayer[50] and associates, in electrolysis studies of $GeCl_4$ in 6N hydrochloric acid reported evidence of an anion which they assumed to be $GeCl_6^{(=)}$. They used the slight solubility of $GeCl_4$ in concentrated hydrochloric acid as a further indication that some chlorogermanic acid may be formed. They further stated that the low solubility of $GeCl_4$ in concentrated hydrochloric acid makes it impossible to achieve any high concentration of $GeCl_4$ in an aqueous solution. Therefore, very little if any germanium exists in solution as the cation.

Pugh[57] has tabulated the solubility of GeO_2 in differing concentrations of hydrochloric acid. He reported that the minimum solubility is in 5.2M acid, and maximum in 7.6M, the strongest acid used.

Allison and Miller[3] determined the solubility of $GeCl_4$ in hydrochloric acid solutions for the concentration range 8 molal to 16 molal acid. They found it to be least soluble in 16.14 molal acid, and the weaker the acid the greater was the solubility found. They compare the low solubility of $GeCl_4$ with the high solubility of $TiCl_4$, $SnCl_4$ and $PbCl_4$ in strong hydrochloric acid solution. They concluded from this analogy that germanium does not form complex chloro acids at this acid strength. The other metals form H_2MeCl_6. Cs_2GeF_6 was prepared by dissolving GeO_2 in hydrofluoric acid and

adding a solution of cesium fluoride.[64]

Cozzi and Vivarelli[17] experimented with reduction of germanium at the dropping mercury electrode. They postulated the existance of germanium as a basic ion at a pH greater than 1, and the presence of $GeCl_3^{(-)}$ at a pH less than 0.5.

Everest and Salmon[22] reported that germanium was adsorbed on an ion exchange column from a solution with a pH of 9. They postulated the formation of $Ge_5O_{11}^{(--)}$ at this pH, and $HGeO_3^{(-)}$ at a higher or lower pH. The latter ion was not appreciably adsorbed.

Lead: Jentzsch and Frotscher[32] list $PbCl_6^{(-4)}$, $PbCl_4^{(-2)}$ and $PbCl_3^{(-)}$ as the chloro complexes of lead. Vasilev and Proukhina[69] postulated the presence of $PbCl_3^{(-)}$ in sodium chloride and potassium chloride solutions. Cavigli[14] reported the formation of $PbCl_4^{(--)}$ in very concentrated solutions of KCl or LiCl.

Zinc: Similar complex ions have been reported for zinc. $ZnCl_4^{(-2)}$, $ZnCl_3^{(-)}$ and $ZnCl_3\ H_3O\ H_2O$ are included in the report of Jentzsch and Frotscher.[32] Stokes,[66] on the basis of the anomolies found in the vapor pressure lowering of mixtures of the zinc halides with alkali metals and magnesium, mentions the formation of $ZnCl_4^{(--)}$. Sillen and Anderson[63] confirmed the existence of $ZnCl_3^{(-)}$ and $ZnCl_4^{(--)}$.

Cadmium: According to Jentzsch and Frotscher[32] cadmium may exist as $CdCl_6^{(-4)}$, $CdCl_4^{(-2)}$ and $CdCl_3^{(-1)}$. Korshunov and associates[36] verified the formation of these ions. Studies by Leden[51] offer evidence for the existence of $CdCl_3^{(-)}$.

The Analytical Chemistry of Germanium

Krause and Johnson[46] gave a good review of the analytical methods available for germanium. The most widely used methods until recently, have been variations of those of Dennis and coworkers.[20][21] Most gravimetric methods involve precipitation of the germanium as GeS_2 with subsequent conversion to GeO_2 before weighing. The methods of conversion vary. Oxidation by nitric acid, and by hydrogen peroxide have been used. Telford and Furman[68] outline an analytical method for germanium in alloys in which germanium is precipitated as a tannin compound and converted to the dioxide by direct ignition.

The oxalate may be precipitated and ignited to GeO_2 also. Other gravimetric methods consist of precipitation as molybdogermanic or tungsto-germanic salts of organic bases, or precipitation as Mg_2GeO_4. For analysis of micro quantities, the gravimetric methods are not suitable because of inherent inaccuracy.

The volumetric methods include the formation of the mannitol-germanium complex with subsequent titration using sodium hydroxide[15]. Treatment of the mannitol-germanium complex with potassium iodide-potassium iodate, and titration of the liberated iodine with sodium thiosulfate is also possible. Alimarin and Alekseeva[2] applied iodometric titration to the precipitate of the oxine salt of molybdogermanic acid. None of these procedures offer a simple method for analyzing germanium in micro quantities.

The limit of accuracy of determination is about one part per million by spectrographic methods. These procedures are limited to definite types of samples.

Bowkley[74] and others have adapted polarographic procedures to the determination of germanium. Accuracy is not good in lower than 10^{-4} molar concentrations.

The colorimetric methods offer the best possibility of accurately determining small amounts of germanium. Various workers have made applications of the yellow color of the molybdogermanium complex and its subsequent reduction to molybdenum blue. The heteropoly blue technique of Boltz and Mellon[5] is an adaptation of this method.

The oxidized hematoxylin procedure of Newcombe[55] and coworkers is available, but requires a careful pH control. Cluley[16] adapted the qualitative phenylfluorone method of Gillis[23] to a quantitative procedure. Schneider and Sandell[61] used an adaptation of this method after CCl_4 extraction of the germanium.

EXPERIMENTAL

The adsorption and elution studies of lead, cadmium, and zinc, previously discussed suggested the possibility of using anion exchange technique for their separation. The evidence for the formation of the chloro germanic complex indicated that this element could also be separated by anion exchange. The solution containing the elements were made 8N-9N with HCl for the sorption step, germanium is quite soluble in this acid concentration and Nelson and Kraus[54] reported that lead is not adsorbed on Dowex 1 under these conditions.

Materials and Equipment

Materials: The germanium dioxide, 98.5% pure, was furnished by the Eagle-Picher Company and corresponded to their electronic grade product.

The Dowex 1-X8 resin was furnished by the Dow Chemical Company and corresponds to their commercial grade product with 8% cross-linkage.

The phenylfluorone (2, 6, 7-Trihydroxy-9-phenyl-3-isoxanthone) was obtained from Eastman Organic Chemicals and was used as supplied.

The gum arabic used with color method was Fisher U.S.P. grade white powder.

The gelatin was Eastman practical grade. The hydrofluoric acid was Baker's A.C.S. standard grade.

All other chemicals were laboratory reagent grade and

were used as received from supplier.

Absolute ethyl alcohol was used for making up the phenyl-fluorone solution.

Equipment: Exax blue line pipets and volumetric flasks were used for all measurements. The same pipet of any given size was used throughout.

The ion exchange columns were made from inner condenser tubes. The lower end was constricted and connected to a 3 inch tygon tube. The flow rate was controlled by a pinch clamp which worked on the tygon tubing. The lower tubing end contained a buret tip.

The dropping mercury electrode consisted of a capillary tube attached to a buret with a side arm near the bottom. A saturated calomel electrode, with a 3% agar saturated potassium chloride salt bridge for making contact with the solution, was used as reference electrode.

The polarograph was the Sargent-Heyrovsky, Model XII photographic recording.

The photoelectric colorimeters used were the Klett-Summerson manufactured by the Klett Manufacturing Company, and the Evelyn Photoelectric Colorimeter manufactured by the Rubicon Company of Philadelphia.

Standard Stock Solutions: Since primary standards for lead and cadmium were not available, electrolytic analyses of their salts were performed before making up standard solutions.

Originally, weak acid solutions of the germanium, zinc, lead, and cadmium were used but these elements did not

remain dissolved. Nine normal hydrochloric acid solutions were found satisfactory since most of our sorptions were from that strength acid. Small amounts of germanium precipitated out of solution after standing 3 or 4 weeks.

Lead Stock Solution: I. For preliminary work the lead solution equivalent to approximately 0.01 g. of Pb/ml. was made by dissolving 16.0026 g. of Mallinkrodt Analytical Reagent lead nitrate in water. Ten drops of concentrated nitric acid was added and the solution diluted to 1000 ml. It was analyzed for lead content by the electrolytic method of Schrenk and Delano[62] and found to contain 0.00997 g. of lead per ml. Special precautions were taken to prevent loss by spraying.

II. For later work, 6.7115 g. of $PbCl_2$ (Baker, C.P.), was dissolved in hot 3-1 hydrochloric acid and analyzed for Pb. One ml. contained 0.01 g. of Pb. Powdered test lead was considered for use in the standard solution but found difficult to dissolve without oxidation.

Germanium Stock Solution: GeO_2, in small amounts, will dissolve in water when allowed to stand 2 or 3 days. Its solution in a minimum amount of dilute sodium hydroxide is more satisfactory.

Ten or fifteen ml. of dilute sodium hydroxide was used to dissolve 0.1463 g. of 98.5% GeO_2 and the solution diluted

to 1000 ml. with 3-1 hydrochloric acid. One ml. contained 100 μg. of germanium. The solution was stored in glass containers and inspected daily. A fresh solution was made every month.

Zinc Stock Solution: A zinc solution was made by dissolving 12.4470 g. of pre-ignited zinc oxide in hydrochloric acid and diluting to 1000 ml. with 3-1 acid. One ml. contained 0.01 g. of zinc.

Cadmium Stock Solution: The cadmium chloride used had to be analyzed for cadmium content before making up the standard solution.

The solution was analyzed by plating it onto copper plated platinum electrodes by the Slomin[65] method of electrodeposition. It was observed that a black oxidation product formed if the electrodes were not kept completely immersed. Check results were obtained by using rotating electrodes at 0.6-0.8 amps. for 6 hours; and still electrodes for 5 hours at 0.6 amps., then at 1½ amps. for 1 hour.

The stock solution was made by dissolving 16.3210 g. of $CdCl_2$, previously dried in an oven at 130°C, in 3-1 hydrochloric acid and diluting to 1000 ml. with the acid. Analysis showed it to contain 0.01003 g. of Cd/ml. The $CdCl_2$ had to be kept well stoppered and hurriedly weighed to prevent moisture uptake.

Column Packing Technique

For exact comparison purposes the resin was dried over

anhydrone before packing. It was found, however, that 5-10% moisture still remained. Dowex 1, as received, gives off gas when first treated with hydrochloric acid. To prevent formation of air pockets in the column the resin was soaked in concentrated hydrochloric acid in a beaker, until fizzing stopped. The excess hydrochloric acid was poured off and the resin was washed 2 or 3 times with distilled water until most of the resin settled. After the floating fines were decanted off, the resin was slurried around and poured directly into the column while the pinch cock was open. Pyrex wool plugs were used above and below the resin. The column was conditioned overnight with approximately 9N or 12N hydrochloric acid before the sorption solution was poured through. Care was taken not to allow the level of the liquid to get below the top of the resin bed.

Analytical Methods

Analytical methods for small amounts of the elements had to be selected. In all cases the existing methods required modification.

Germanium: A modification of the method by Cluley[16] was developed for germanium. The method was satisfactory for as little as 0.04 P.P.M. of this element.

The phenylfluorone solution was made up according to the original method of Cluley.[16] A control standard containing the same amount of germanium as the amount expected in the sample of highest content was run with all samples. An

approximate analysis for acidity was run on all samples before testing for germanium. Color developments were made in 50ml. volumetric flasks as follows:

(1) An aliquot containing not over 20 μg. of germanium was pipetted into the 50ml. volumetric flask.

(2) Enough hydrochloric acid was added to the flask until it contained the equivalent of 5 ml. of 9N acid.

(3) Water was added to raise the liquid volume to 20 ml.

(4) Five ml. of 0.5% gum arabic solution was added.

(5) Fifteen ml. of phenylfluorone (75 mg. in exactly 250 ml. of EtOH containing 12 ml. of 3N-HCl) was added.

(6) Flasks were carefully filled to the 50 ml. mark with EtOH.

(7) Samples were shaken throughly, and immediately set in a cool water bath at 20° or below.

(8) Solutions were shaken every 10 minutes and removed from the water bath at the end of 30 min.

(9) Flasks were again filled to the 50 ml. mark with EtOH and shaken every 10 minutes for another 30 min.

(10) By use of a blank and standard, color development was read on the Evelyn, or Klett Summerson photoelectric colorimeter, using a green 500 or 515 m filter.

Lead: A polarographic method was adapted for lead.

Lead has a half-wave potential of -0.435V in 1N hydrochloric acid. Since the concentration of supporting electrolyte is so high compared to the concentration of lead, a 10% error in amount of supporting electrolyte has negligible effect.

(1) The approximate acid concentration of the solution to be analyzed was determined by titrating against 1.06N potassium hydroxide. Phenolphthalein was used as indicator. Once the acid strength of a given elution fraction had been determined, it was not necessary to analyze the corresponding fraction from every experiment as long as the same column was used.

(2) An aliquot of the solution was taken and sufficient hydrochloric acid was added so that when diluted to 100 ml. it would be 1N in acid concentration.

(3) Ten ml. of 1% gelatin solution was added and the aliquot diluted to 100 ml. with distilled water.

(4) A polarogram was recorded using a dropping mercury cathode and saturated calomel electrode.

The method can detect as little as 0.0005 g. of lead based on content in the original solution of 100 ml., from which an aliquot was taken.

Zinc and Cadmium: Polarographic methods were also adapted for the analysis of zinc and cadmium. Zinc and cadmium were first analyzed polarographically in 0.1N potassium chloride solution. This was abandoned when it proved difficult to keep zinc in solution at the neutral

point. Addition of acid to dissolve it would cause overlapping of the H^+ and Zn^{++} reduction waves. The solutions were analyzed for zinc and cadmium by recording polarograms on an aliquot adjusted to 1N NH_4OH + 1N NH_4Cl with 10N NH_4OH and 5N NH_4Cl solutions. the method gave excellent analytical results. Cadmium has a half-wave potential of -0.81V. and zinc -1.36V. They were analyzed in the same polarographic solution from the same curve. As much as 10% variation in supporting electrolyte concentration has little effect on the accuracy.

Preliminary Experiments

Preliminary experiments were run using fast elution rates and large diameter columns.

Two columns were prepared. One contained 20-50 mesh resin and the other 50-100 mesh resin. As a rough approximation the amount to use was based on the total capacity of resin expressed by the manufacturer. This does not take into consideration the break through capacity. As designated by the manufacturer the 20-50 mesh resin has a capacity of 0.3 meq./2.7 g. and the 50-100 mesh of 0.3 meq./2.7 g. on an oven dry basis. Fifty ml. of each air dried resin was used to prepare the preliminary columns. The following procedure was followed:

(1) The solution to be analyzed was titrated against standard base to determine acid concentration.

(2) An aliquot was taken and enough 10N NH_4OH added to neutralize the HCl and be enough in excess so

final volume would be 1N in NH_4OH.

(3) Enough additional NH_4Cl was added so that the final NH_4Cl concentration would be 1N.

(4) 10 ml. of 1% gelatin was added and the solution made up to 100 ml. with distilled water. After passage of nitrogen a polarogram was recorded using a dropping mercury cathode and saturated colomel anode. The method can detect as little as 0.0001 g. of zinc or cadmium based on content in original solution of 100 ml., from which an aliquot was taken.

The columns were conditioned overnight in concentrated hydrochloric acid.

Since Nelson and Kraus[54] had found that Dowex 1 does not adsorb lead in 8N or stronger hydrochloric acid, it was decided to use approximately 8N acid for the adsorptions. Another possibility when working with lead alone would have been to adsorb it in 1.5N hydrochloric acid and elute with a very weak hydrochloric acid solution. For chromatographic separations involving several ions, however, this doesn't offer a wide enough range between acid adsorption and elution strength.

Procedure: A solution containing 500 μg. germanium, 0.05 g. lead, 0.05 g. zinc and .05 g. cadmium was made by adding 5 ml. of each stock solution to a 100 ml. volumetric flask and filling to the mark with approx. 8N hydrochloric acid.

Since the free column space above the resin was only

30 ml. the sorption solution was poured in as the solution level fell. A drop-size calibration was made and the rate controlled by counting and timing with a stopwatch. Within limits the rate could be controlled by opening or closing the pinch cock.

The level of the sorption solution was allowed to fall just below the top of the glass packing, at which time a 2 or 3 ml. portion of acid, of sorption acid strength, was added. Three or four portions of this size were added and the level of the solution allowed to drop each time; thus the diffusion of ions from the sorption solution into the wash solution was decreased.

The sorption solution was always followed with a large volume of sorption strength acid. This insured complete wash through of the lead from the interstitial spaces. The level of the sorption solution and subsequent elution solutions were always allowed to fall below the top of the pyrex wool plug before the following elution was made. A large increase in acid strength of the following elution solution, due to diffusion, was thus prevented.

The sorption and elution rates throughout are based on actual volume rather than ml. sq. cm.$^{-1}$min.$^{-1}$ which is sometimes used. Adjustment to rate/cross sectional area may be made by dividing the rates given by the cross sectional area of the column.

Hydrochloric acid of approximately 3N, or approximately 4N, strength was used as a starting concentration for the elution of germanium. Approximately 0.01 normal acid was

used to elute zinc and, approximately 0.001 normal acid to elute the cadmium. The column was washed with a large volume of distilled water before reconditioning for the following experiment.

Tables (1-5) show some of the results obtained in preliminary experiments. A complete analysis of all fractions was not made.

In all the following trials:

(1) The resin consisted of 50 ml. of air dried Dowex 1-X8, 20-50 mesh, or 50-100 mesh.

(2) The column of resin was 2 cm. in diameter and 25 cm. long.

(3) The sorption solution contained 500 μ g. germanium, 0.05 g. lead, 0.05 g. Zn, and 0.05 g. cadmium.

TABLE I

RESULTS OF FIRST PRELIMINARY EXPERIMENT

Resin Size - (20-50 mesh)

Steps	HCl Concentration	Volume Used ml.	Flow Rate ml./min.	Analysis Ge- μg. others mg.	Per cent of Total Amount Added
Sorption	2-1 (approx. 8N)	100	25	Pb-44.2 Ge-80	88.4 16
Elution 1	1-2 (approx. 4N)	200	25	Ge-380	76
Elution 2	approx. 0.01N	200	25	Ge-43 Zn-24.4 Cd-6.2	8.6 48.8 12.4
Elution 3	approx. 0.001N	200	25	Zn-15.9 Cd-13.2	31.8 26.4
Elution 4	Water	not analyzed			

% of total, recovered	Lead	Germanium	Zinc	Cadmium
	88.4%	100.6%	79.6%	38.8%

The sorption step was followed by washing column with 100 ml. of 8N HCl.

Remainder of zinc and cadmium was probably in water elution made after other elutions.

TABLE II

RESULTS OF SECOND PRELIMINARY EXPERIMENT

Resin Size - (50-100 mesh)

Steps	HCl Concentration	Volume Used ml.	Flow Rate ml./min.	Analysis Ge-mg. others mg.	Per cent of Total Amount Added
Sorption	2-1 (approx. 8N)	100	25	Pb-47.4 Ge-none	94.8
Elution 1	1-2 (approx. 4N)	200	25	Ge-443	88.6
Elution 2	approx. 0.01N	200	25	Ge-none Zn-36 Cd-trace	72
Elution 3	approx. 0.001N	200	25	Cd-22	44
Elution 4	Water	Not analyzed			

	Lead	Germanium	Zinc	Cadmium
Per cent of total, recovered	94.8	88.6	72.0	44.0

The sorption step was followed by washing column with 100 ml. of 8N HCl.

Pressure was used to maintain flow rate.

TABLE III

RESULTS OF THIRD PRELIMINARY EXPERIMENT

Resin Size (20-50 mesh)

Steps	HCl Concentration	Volume Used ml.	Flow Rate ml./min.	Analysis Ge- µg. others mg.	Per cent of Total Amount Added
Sorption	2-1 (approx. 8N)	100	7	Pb-41.1	82.2
Elution 1	1-2 (approx. 4N)	200	7	Ge-400 Pb-5.4 Cd-trace Zn-trace	80.0 10.8
Elution 2	approx. 0.01N	200	7	Ge-19.1	3.8
Elution 3	approx. 0.001N	200	7	Ge-0 Zn-9.9 Cd-23.4	 19.8 46.8
Elution 4	Water	not analyzed			

Per cent of total, recovered	Lead	Germanium	Zinc	Cadmium
	93.0	83.8	74.6	48.4

The sorption step was followed by washing column with 100 ml. of 8N HCl.

TABLE IV

RESULTS OF FOURTH PRELIMINARY EXPERIMENT

Resin Size (20-50 mesh)

Steps	HCl Concentration	Volume Used ml.	Flow Rate ml./min.	Analysis mg.	Per cent of Total Amount Added
Sorption	3-1 (approx. 9N)	100	8	Pb-47.4 Zn-0 Cd- 3.25	94.8 6.5
Elution 1	1-3 (approx. 3N)	200	8	Pb-2.1 Zn-0 Cd-0.25	4.2 0.5
Elution 2	approx. 0.01N	200	8	Pb-0 Zn-32.9 Cd-6.2	 65.8 12.4
Elution 3	approx. 0.001N	200	8	Pb-0 Zn-8.1 Cd-21.8	 16.2 43.6
Elution 4	H_2O	100	8	Pb-0 Zn-3.6 Cd-14.5	 7.2 29.0

Per cent of total, recovered	Lead	Zinc	Cadmium
	99.0	89.2	92.0

The sorption step was followed by washing column with 100 ml. of 9N HCl.

TABLE V

RESULTS OF FIFTH PRELIMINARY EXPERIMENT

Resin Size (20-50 mesh)

Steps	HCl Concentration	Volume Used ml.	Flow Rate ml./min.	Analysis mg.	Per cent of Total Amount Added
Sorption	3-1 (approx. 9N)	100	8	Pb-50 Cd-3.2 Zn-0	100 6.4
Elution 1	1-3 (approx. 3N)	225	8	Pb Zn-0 Cd	
Elution 2	approx. 0.005N	225	8	Pb-0 Zn-32.7 Cd-13.1	65.4 26.1
Elution 3	approx. 0.0001N	225	8	Pb-0 Zn-10.7 Cd-20.6	21.4 41.2
Elution 4	H_2O	250	8	Pb-0 Zn-3.2 Cd-11.1	6.4 22.2

Per cent of total, recovered	Lead	Zinc	Cadmium
	100	93.2	89.6

The sorption step was followed by washing column with 125 ml. of 9N acid.

The interstitial resin space was determined and found to be 30 ml. Twenty ml. of solution were allowed to run through before changing to collect new elution fraction.

The method used throughout for determining interstitial resin space was as follows:

(1) To approximately 20 ml. of distilled water 20 drops of concentrated NaOH, and phenolphthalein were added.

(2) With distilled water in the resin bed, strong hydrochloric acid was added to the column.

(3) The amount of solution collected from bottom of column, before pink color of phenolphthalein disappeared, was measured.

(4) For a safety margin 5-10 ml. was subtracted from volume caught before using results obtained.

Conclusions from Preliminary Experiments

(1) Germanium will adsorb onto Dowex 1 in 8 or 9N hydrochloric acid solution.

(2) A large per cent of the germanium adsorbed can be eluted with 3-4N hydrochloric acid with little or no contamination from other ions.

(3) The results for the separation of cadmium and zinc were not good, but it was believed that the method could be improved by changing the technique and acid concentrations.

Cadmium in the lead, sorption, fraction seemed to indicate that the break through capacity of the column had been exceeded. The amount of zinc and cadmium to be used in all following sorption fractions was changed to 0.01 g. of each. The break through capacity of the resin for ger-

manium was determined.

Procedure for Determining Break-through Capacity: The 20-50 mesh resin was dried 2 weeks over silica gel and $CaCl_2$. The 50-100 mesh was screened to remove all particles less than 100 mesh. It was dried 2 weeks over anhydrone. The sorption solution contained 10 mg. of germanium per 1,000 ml. of 9N HCl solution.

(1) A column of each size resin was prepared from 5 g. of dry resin. The size of the large mesh column was 12 x 125 mm. The small mesh column was 12 x 120 mm. Both sizes were measured while in strong hydrochloric acid. The interstitial volume of each was found to be 5 ml.

(2) The columns were conditioned in concentrated hydrochloric acid for 3 hours.

(3) The germanium solution was adsorbed from 25 ml. aliquots which contained 250 μg. of germanium per aliquot. Four ml. of interstitial solution was collected, and followed by a 4 ml. overlap.

(4) Sorption rate was 1 ml./min.

(5) To remove interstitial germanium each aliquot was followed by a washing step of 25 ml. of 9N hydrochloric acid for the first four aliquots, and 10 ml. thereafter.

(6) Each aliquot and its washing were collected in a 50 ml. volumetric flask and made up to volume before testing. No germanium could be detected from either column after the adsorption of the

first four aliquots.

One thousand μg. were adsorbed before a break through occurred. The fifth aliquot collected from the large resin column contained 23 g. of germanium. The fifth aliquot from the small resin column contained 16 g. of germanium. The total capacity of the column was not determined, because only its separation ability was of interest. Results of the experiment are shown in Table VI.

TABLE VI

BREAK THROUGH OF GERMANIUM FROM DOWEX 1 COLUMN

Aliquot	Unadsorbed Ge, µg., 20-50 mesh resin	Unadsorbed Ge, µg., 50-100 mesh resin
1-4	0	0
5	23	16
6	39	-
7	78	31
8	62	47
9	92	92
10	100	108
11	108	158
12	125	217
13	133	217
17	172	-
18	164	-
20	179	218

In the absence of lead, zinc, and cadmium, several 100% adsorptions with 100% elutions of germanium were made from longer columns. Eight or nine normal acid was used for adsorption and three or four normal acid was used for elution. Some complete adsorptions and elutions were achieved using both large and small resin columns. Sorption and elution rates were 1 ml./min. Results of two experiments are shown in Table VII. Complete recovery of germanium was not always attained, however the recovery was usually over 90%.

TABLE VII

Results of Sorption and Elution of Germanium in the Absence of Lead, Zinc and Cadmium

	20-50 mesh resin	50-100 mesh resin
Amount of resin:	50 ml. air dried	50 ml. air dried
Column:	Condenser tube	Condenser tube
Packed Column Size:	1 cm. x 45 cm.	1 cm. x 45 cm.
Ge content of solution:	1000 µg.	1000 µg.
Sorption Solution:	9N-HCl	9N-HCl
Per cent Adsorbed	100	100
Eluted with:	200 ml. 3N HCl	200 ml. 3N HCl
Per cent eluted	100	100

Effect of Hydrochloric Acid Strength on the Elution of Germanium: The effect of acid strength on the elution of germanium in the presence of lead, zinc, and cadmium was determined. All adsorptions were made from 8.5N hydrochloric acid solutions containing 500 μg. of germanium, 0.05 g. of lead, and .01 g. each of zinc and cadmium. After the germanium elution the zinc was eluted with 100 ml. of 0.01N-HCl and the cadmium with 250 ml. of water. Each fraction was tested for germanium only. A control standard was used as reference with all analyses. The elution acid strength was determined by titration against 1.08N-KOH. 50-100 mesh Dowex 1 was used. The size of the packed column was 1 cm. x 45 cm. All sorption and elution rates were 1 ml./min. The results for the recovery of germanium by elution with various concentrations of hydrochloric acid are shown in Table VIII.

TABLE VIII

Effect of Varying Hydrochloric Elution Acid Strength in the Elution of Germanium from 50-100 Mesh Dowex 1, in the Presence of Lead, Zinc and Cadmium

	Per Cent of Germanium Recovered				
Acid strength	1.8N	Approx. 2.8N	3.8N	4.9N	5.9N
(Lead) Sorption Fraction	0	0	0	2	0
Germanium Fraction	77.2	80	83.2	36	0
Zinc Fraction	0	0	0	51.8	79.2
Cadmium Fraction	0	0	0	2	5.4
Total	77.2	80.0	83.2	92.0	84.6

The Effect of Variables in Column, Sorption, and Elution Technique: Other variations were used in making additional determinations endeavoring; (1) to get consistent 100% germanium recovery free from lead, zinc, or cadmium, (2) to get complete separation of lead, zinc and cadmium. In each experiment the sorption solution contained .05 g. of lead, .01 g. of zinc, .01 g. of cadmium, and 500 μg. of germanium. Columns were conditioned overnight in 9N-HCl. Twenty ml. overlap to take care of interstitial volume was used in most cases. All fractions were tested for germanium. Fractions were not tested for the other constituents unless germanium recovery was good.

The principal variable factor is underlined in the following summaries:

(1) Column: 20 g. of 50-100 mesh resin, 1 x 40 cm.
Sorption Solution: .05 g. of lead and 500 g. of germanium, in 9N HCl.
Elution: Germanium was eluted in three 50 ml. fractions. Approximately 3N HCl concentration was used for elution of the first two fractions, followed by a 50 ml. fraction using approximately 2N acid. The germanium recovered was 83% of the total, all in the first 50 ml. fraction.

(2) Column: (A) 20 g., 50-100 mesh resin, 1 x 40 cm.
Sorption Solution: 500 μg. germanium, .05 g. Pb in 50 ml. 9N HCl.
Elution: Ge was eluted in three steps: (1) 50 ml. 3N-HCl, (2) 50 ml. 3N-HCl, (3) 50 ml. water.

Elution rate: 1 ml./min.

Analysis showed 100% germanium recovery in 1st fraction. Approximately 3% of total was in other fractions. Total recovery, as analyzed, was 103%.

(B) Conditions in (A) were duplicated. Tests showed 97.6% of germanium in 1st elution, 1% in 2nd elution, and 3% in water elution. Total recovery as analyzed was 101.6%.

(C) Conditions in (A) and (B) were duplicated. Tests showed 100% germanium recovery in 1st elution and 2% in water elution. Analytical results were obtained using both Evelyn and Klett Summerson colorimeters.

(3) Column: 20 g. 50-100 mesh resin, 1 x 45 cm.

Sorption Solution: 500 μg. germanium, .05 g. Pb, .01 g. Zn, .01 g. Cd in 50 ml. 9N-HCl.

Elution: Ge-50 ml. 3N HCl, Zn-50 ml. .01N-HCl, Cd-50 ml. 0.005N HCl, all at a flow rate of 1 ml./min.

Germanium found in each fraction was: Sorption - 3.6%; Ge - 93.6%; Zn - 3%; total 100.2%

(4) Column: Conditioning and sorption solution same as (3).

Elution: Ge - 75 ml. 3N HCl; Zn - 50 ml. .01N HCl; Cd - 100 ml. H_2O.

The per cent of germanium found in each fraction was: Sorption - 11%; Ge - 88.6%; Zn - 4%; total - 103.4%

(5) Column: Conditioning and sorption solution same as (3) and (4).

Elution: Same as (4).

After making elutions in which only 80% of the germanium could be accounted for, 3N - HCl was allowed to remain on the column overnight. Analysis of the solution showed no additional germanium recovery.

(6) Column: Conditioning and sorption solution same as (3), (4), and (5).

Elution: Same as (4) and (5).

The percent of germanium found in each fraction was: Sorption - 0%; Ge - 92%; Zn - 0%; Cd - 5%. Total recovered was 97.0%. Two Ge control standards were used. Immediately before color development one was filtered through 4 pieces of fine grade filter paper. Both standards gave same color development.

Conclusion: No large particles had been formed by hydrolysis of standard solution.

(7) Column: New resin with same column size, conditioning and sorption solution same as (6).

Elution: Ge- 100 ml. 3N HCl at flow rate of 2 ml./min.; Zn - 100 ml. .01N HCl; Cd -210 ml. H_2O. The per cent of germanium found in Ge fraction was 87, none was found in other fractions.

(8) Column: Conditioning and sorption solution same

as (7).

Elution: Ge - 150 ml. 3N acid at flow rate of 2½ ml./min., collected in 100 ml. and 50 ml. fractions; Zn - 100 ml. .01N HCl; Cd - 205 ml. water. The amount of germanium found in 1st 100 ml. Ge fraction was 94.4%, none in other fractions.

(9) Column: Conditioning and sorption solution same.
Elution: Ge - eluted at a flow rate of 2.2 ml./min. using 150 ml. of 4N HCl. Collected in 100 ml. and 50 ml. fractions; Zn - 100 ml. .01N HCl; Cd - 205 ml. H_2O. The recovery of germanium in 1st Ge fraction was 96.2%. None was in other fractions.

(10) Same as previous experiment except Ge was eluted by backwashing. Ninety-one per cent of Ge was recovered in 1st 100 ml. Ge. fraction, none in others.

(11) Column: Same as (10) but enclosed in condenser jacket through which hot water was circulated during germanium elution.
Elution: Ge - 100 ml. 4N HCl, maintained at 55 - 60°C, at flow rate of 3 ml./min; Zn - 100 ml. 0.01N HCl, at a flow rate of 1 ml./min; Cd - 200 ml. water.
Eighty-six per cent of the Ge was recovered in Ge fraction, none in others.

(12) New Column: Condenser tube coated inside with

paraffin and packed with 20 g. of air dried 50-100 mesh resin.

Column size: Approximately same as (11); a cotton plug was used instead of pyrex wool.

Sorption: No change.

Elution: Ge - 100 ml. 0.5N HF in 4N HCl. Flow rate 2 ml./min; Zn - 100 ml. .01N HCl; Cd - 250 ml. H_2O.

HF interfered with germanium analysis.

(13) Column same as previous.

Sorption: No change.

Elution: Ge - 100 ml. 0.1N HF in 4N HCl at flow rate of 2 ml./min.; Zn - 100 ml. 0.01N HCl; Cd - 250 ml. H_2O.

It was determined that analysis could be made for germanium in the presence of lower concentrations of HF. Per cent of Ge recovered in Ge fraction - 76.1%; in Zn fraction 6.4%. Total Ge recovered was 82.5% of total.

(14) New longer column: 25 g. air dried 20-50 mesh resin.

Column size: 1 x 52 cm.

Sorption and Sorption Solution: Same.

Elution: Ge - 6 ml./min. with 4N HCl. Collected 3-100 ml. fractions; Zn - 100 ml. 0.01N HCl, rate 1 ml./min.; Cd - 250 ml. H_2O at 1 ml./min.

The germanium recovered was 86.2% in 1st Ge elution, 8% in 2nd, and none in others.

(15) Column: 25 g. air dried 20-50 mesh resin.
Column size: 1 x 52 cm.
Sorption Solution: 0.05 g. Pb, 500 μg. Ge, 0.01 g. Zn, 0.01 g. Cd, in 50 ml. 9N HCl. Permitted to stand in 9N HCl for 1½ hours after sorption before elution.
Elution: Ge - 100 ml. 3N HCl at 2 ml./min.; Zn - 100 ml. 0.01N HCl at 1 ml./min.; Cd - 250 ml. H_2O at 1 ml./min.
Ninety-nine percent of the germanium was recovered in germanium fraction with none in others.

(16) Column: (A) New 20 g. air dried 50-100 mesh resin with fines screened out.
Column size: 1 x 45 cm.
Sorption: 0.05 g. Pb, 1000 μg. Ge, .01 g. Zn, .01 g. Cd in 50 ml. 9N HCl.
Elution: Ge - 100 ml. 3N HCl at rate of 2 ml./min. Zn - 100 ml. 0.01N HCl at rate of 1 ml./min.; Cd - let water stand on column 12 hours before eluting with 250 ml. water.
Ge recovered in Ge fraction was 87.4%. None was in other fractions.
(B) Same as (A) except 20-50 mesh resin column was used.
Ge recovered in Ge fraction was 90.4%, none in other fractions.
Complete separation of Ge, Pb, Zn and Cd was accomplished for (A). Better than 99% recovery of

the Pb, Zn, and Cd was obtained.

Recommended Procedure for Separating Lead, Germanium, Zinc and Cadmium: The best results were obtained by using the following procedure:

Sorption Solution: 0.05 g. Pb, 500 μg. Ge, 0.01 g. Zn, 0.01 g. Cd in 50 ml. of 3-1 HCl, approximately 9N.

(1) The sorption solution was poured into the top of column. The first 15 ml. from column was discarded because of interstitial space. Fifteen ml. overlap was maintained throughout. Sorption rate was 1 ml./min.

(2) After level of sorption solution had fallen below pyrex plug, four-5 ml. portions of 9N HCl were added allowing level to drop after each addition. Thirty ml. additional of 9N HCl were passed through at 1 ml./min. to remove lead from interstitial space.

(3) Germanium was eluted with 50 ml. of approximately 3N HCl at 1 ml./min.

(4) Zinc was eluted with 50 ml. of approximately 0.01N HCl at 1 ml./min.

(5) Cadmium was eluted with 250 ml. of distilled water at 1 ml./min. It was found that in order to consistently obtain complete cadmium elution, 250 ml. elution volume was required.

Germanium was tested for by the phenylfluorone method. Recovery of germanium in one fraction

was verified by check analysis on both the Evelyn and Klett-Summerson colorimeters.

The successful separations of lead, germanium, zinc, and cadmium are shown in Table IX. All of the lead, zinc, and cadmium fractions were not analyzed for these respective elements but were analyzed for germanium. The recorded polarograms for the separation and analysis of lead, zinc, and cadmium are shown in Figures 1 through 5.

TABLE IX

RECOVERY OF LEAD, GERMANIUM, ZINC AND CADMIUM OBTAINED IN SUCCESSFUL SEPARATIONS

Experiment No.	Lead, Per cent	Germanium, Per cent	Zinc, Per cent	Cadmium, Per Cent
1	-	83	-	-
2 A.	97	100	-	-
B.	100	97.6	-	-
C.	100	100	-	-
3	95	93.6	94	40
6	-	92.0	-	-
7	-	87.0	-	-
8	-	94.4	-	-
9	100	96.2	100	97
10	-	91.0	-	-
11	-	86.0	-	-
14	-	86.2	-	-
15	97.0	99.0	96	98
16 A.	100	87.4	100	100
B.	-	90.4	-	-
Additional Experiment Using Recommended Procedure	100	100	100	100

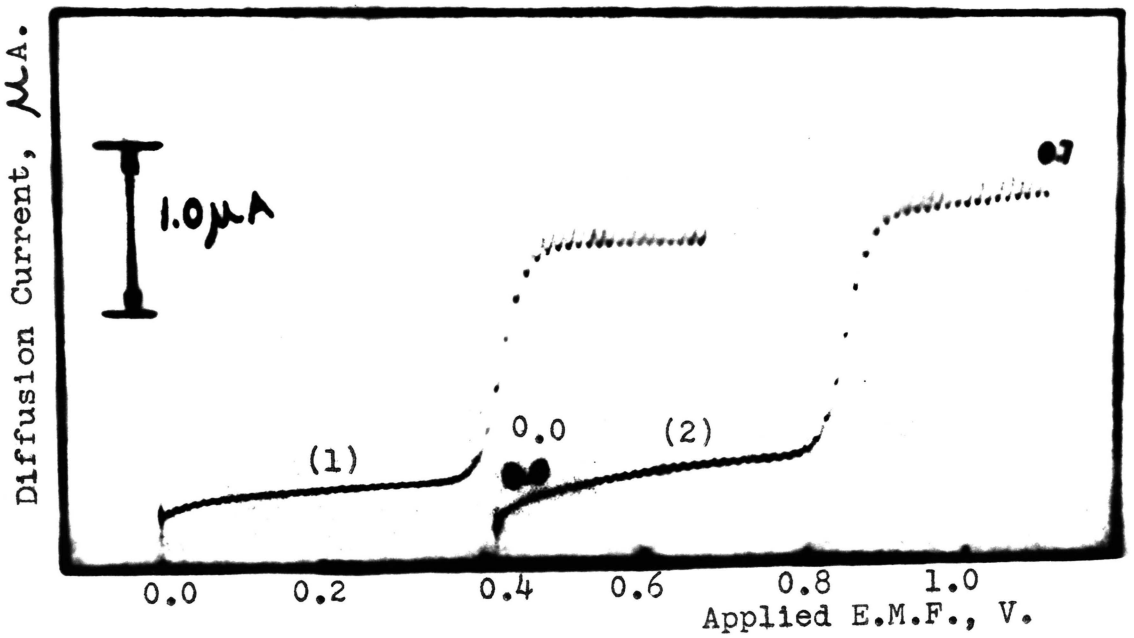


Figure 1.

Polarogram Showing Recovery of Lead in Sorption Fraction

(1) Lead standard containing lead equivalent to 0.05 g.

(2) Lead in sorption fraction.

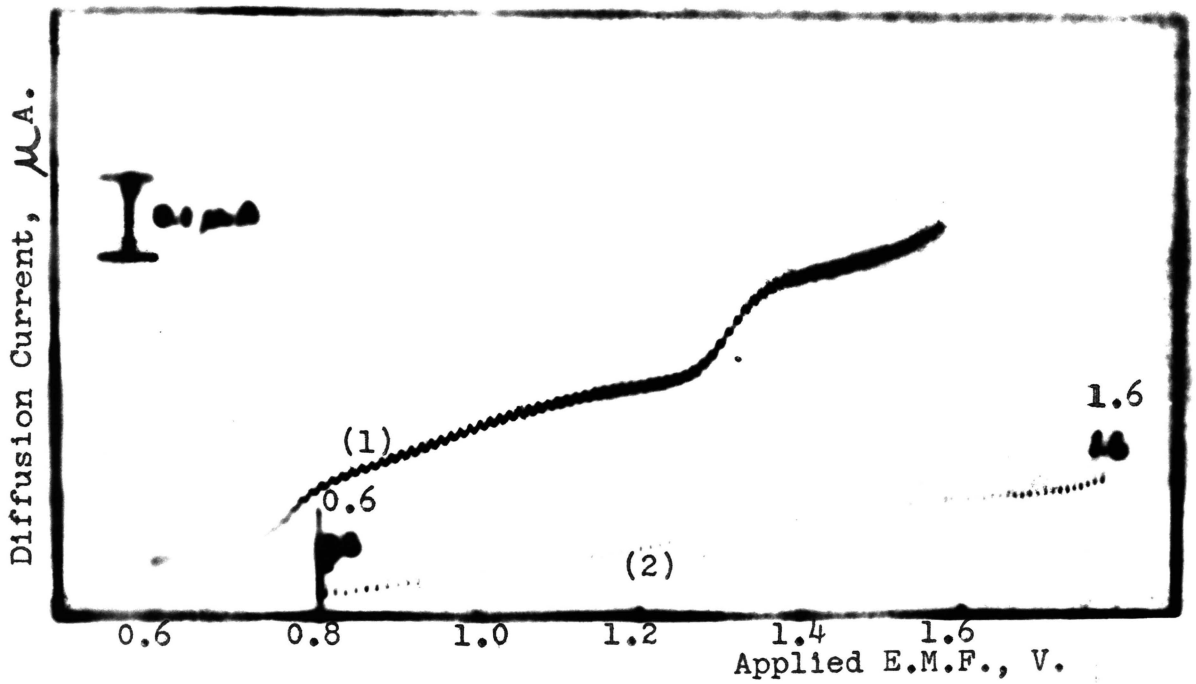


Figure 2.

Polarogram Showing Absence of Zinc and Cadmium in Lead Fraction

(1) Zinc and cadmium standard containing zinc and cadmium equivalent to 0,001 g. of each.

(2) Zinc and cadmium in lead fraction.

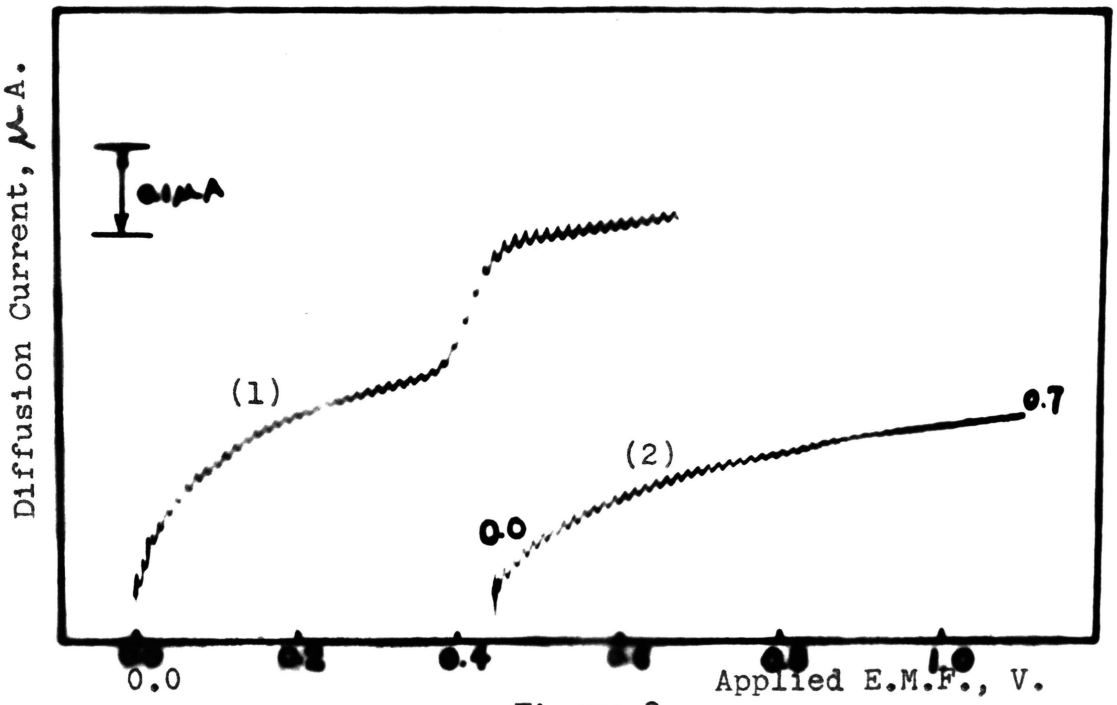


Figure 3.

Polarogram Showning Absence of Lead in Germanium Fraction

(1) Standard, containing lead equivalent to 0.005 g.

(2) Lead in germanium fraction.

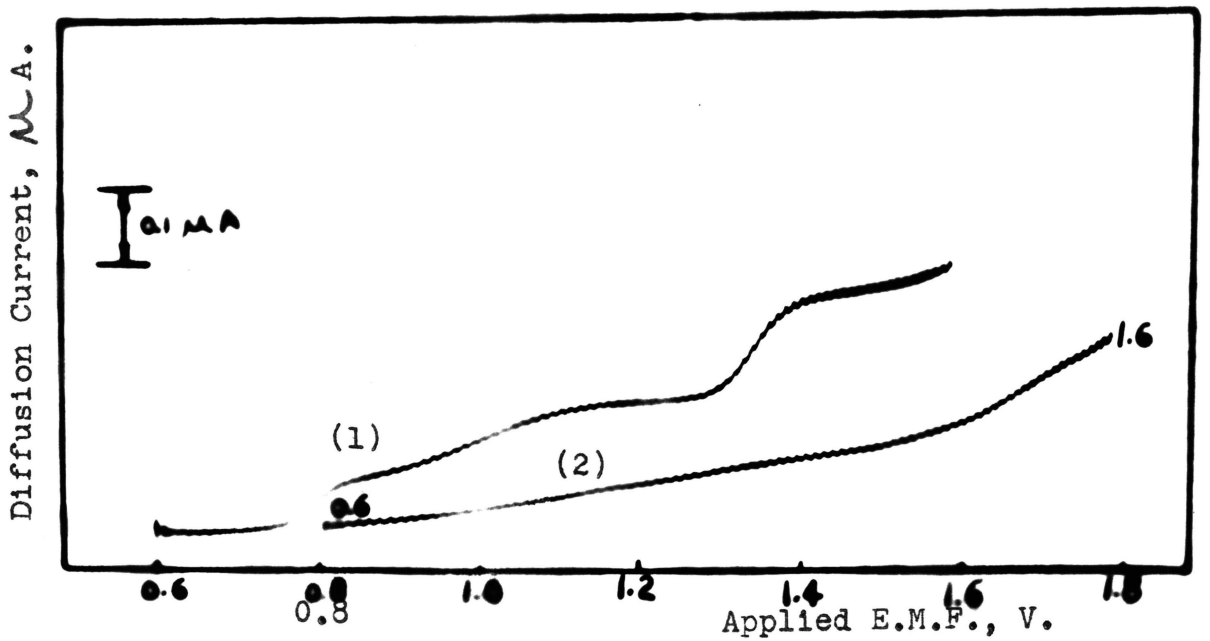


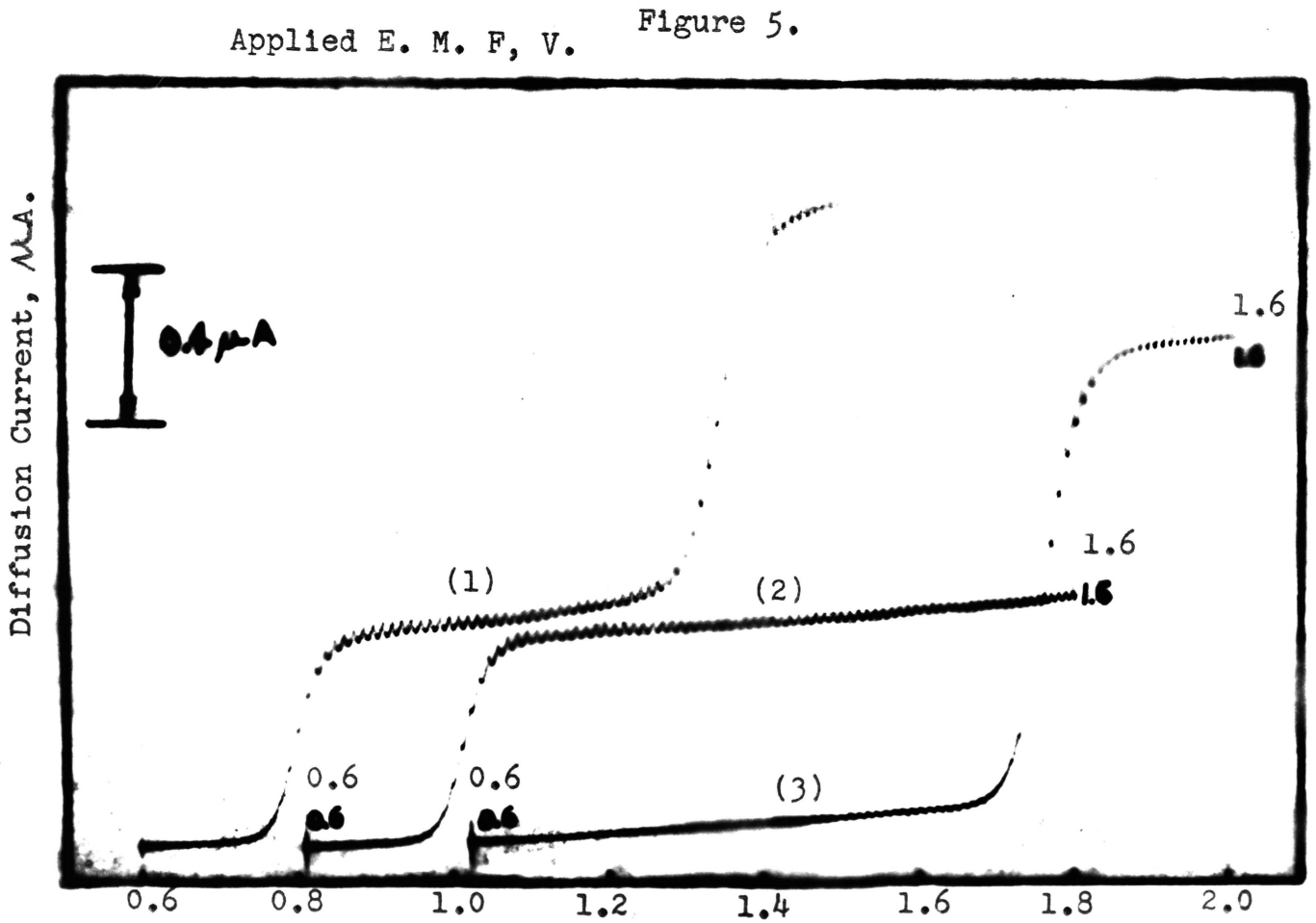
Figure 4.

Polarogram Showing Absence of Zinc and Cadmium in Germanium Fraction

(1) Zinc-cadmium standard containing zinc and cadmium equivalent to 0.001 g. of each.

(2) Zinc and cadmium in germanium fraction.

Figure 5.



Polarogram Showing Recovery of Zinc and Cadmium in their Respective Fractions

(1) Zn - Cd standard containing zinc and cadmium equivalent to 0.01 g. of each.

(2) Cadmium and zinc in cadmium fraction.

(3) Cadmium and zinc in zinc fraction.

CONCLUSIONS AND DISCUSSION

Germanium can be adsorbed onto Dowex 1 from 8 - 9N HCl solution.

Germanium can be eluted from Dowex 1 with 3 - 4N HCl. Consistent 100% recovery was not proved. Lack of consistent recovery could have been due to: (1) Resin effect, which interfered with analysis by preventing complete development of phenylfluorone color; (2) Colloidal formation of the germanium due to hydrolysis, before, after, or during adsorption or elution; (3) Part of germanium being readsorbed as another anion; (4) Inefficiency of the method for germanium analysis.

Germanium, lead, zinc and cadmium can be separated by anion exchange. Recovery of lead, zinc and cadmium was better than 99%.

The method is too slow for routine work if separation of all constituents is desired. Twelve hours are required for sorption and complete elution.

Results indicate that by use of a shorter column with a larger diameter, germanium may be rapidly separated from lead, zinc, and cadmium by anion exchange in 45 minutes or less, if separation of the other constituents is not desired. Experiments showed that germanium can be eluted in 15 - 20 minutes.

In addition to the ions mentioned by Cluley, and Schneider and Sandell, which interfere with the color development of phenylfluorone, Pb (IV) should be added. The

$PbCl_6^{=}$ complex was found to give a rapid and intensive color development. (See Appendix)

Further proof is offered that germanium exists as a chloro-germanic anion in strong hydrochloric acid solution. Adsorption and elution results indicate a transition at 5 - 6 normal acid strength to some other ion species or compound of germanium.

Slow hydrolysis of germanium occurs even in 9N hydrochloric acid.

There is a need for the developement of a better method for germanium analysis, expecially in low concentrations. Most colorimetric methods of analysis have an accuracy of $\pm$ 2.5 per cent. It is doubtful that the phenylfluorone method will give this accuracy. It is believed that results reported in this investigation for 95 - 96% recovery of germanium are good.

SUMMARY

1. The anion exchange behavior of germanium was studied.
2. A method was devised for the separation of germanium, lead, zinc and cadmium by anion exchange.
3. Studies were made on the phenylfluorone method of germanium analysis.
4. Changes were made in the Cluley phenylfluorone method of germanium analysis, which make it more widely applicable.
5. A literature review on the theory and practice of anion exchange chromatography was given.

APPENDIX I

Some Notes on the Phenylfluorone Method for Germanium Determination

1. The phenylfluorone color development with germanium failed to conform to Beer's Law for as high a concentration as the results reported by Cluley. The highest concentration at which it conformed was 0.4 p.p.m. The data listed below indicate that there is non-conformity to Beer's Law in the higher concentration range. The Evelyn colorimeter was used to check these results.

Germanium P.P.M.	Klett-Summerson Reading	Scale Reading per 0.02 P.P.M.
0.04	6	3.0
0.08	12	3.0
0.12	16	2.7
0.16	23	2.9
0.20	30	3.0
0.40	56	2.8
0.60	66	2.2
0.80	80	2.0
1.0	91	1.8

2. The phenylfluorone we obtained did not dissolve in hydrochloric acid, as advised by Schnieder and Sandell. The solution method of Cluley was used.

3. The Pb^{+4} ion will cause a color reaction with phenylfluorone. This was brought to our attention through the

anomolous results obtained in the analysis for germanium when $PbNO_3$ and a small amount of HNO_3 was present. If the lead sorption, fraction was tested within 30 minutes after coming through the column little germanium was found. When the same solution was tested after 2 or 3 hours a positive germanium test resulted. If all solutions were not tested for germanium immediately, more than 100% germanium recovery resulted, according to analysis.

Periodic color comparisons were made on two 100 ml. 9N HCl solutions. One contained 0.05 g. of lead as the nitrate and 8 - 10 drops of concentrated nitric acid. The other contained 1000 µg. of germanium. After a given time was allowed for lead oxidation, color intensity measurements were made. The results are shown in the following table:

Color Development Was Started After	Germanium Solution Color Intensity, E	Lead Solution Color Intensity, E
10 min.	0.2788	0.0300
40 min.	0.2900	0.0300
24 hrs.	0.2788	0.0792
72 hrs.	0.3010	0.3474

Lead chloride in strong hydrochloric acid developed no color with phenylfluorone even after standing several days. In the lead nitrate solution, the nitrate ion probably reacts with HCl to release Cl_2. In solution some HOCl is formed. The Pb (II) is oxidized to Pb (IV) which gives a color on reaction with phenylfluorone. In 9N - HCl, formation of $PbCl_6^{(=)}$ is possible. Since a selected filter was

used, it is not likely that the large increase in adsorption was due to the actual yellow color of H_2PbCl_6.

Chlorine was bubbled through a $PbCl_2$ solution in concentrated hydrochloric acid. The yellow color of H_2PbCl_6 was evident. A rapid intensification of the phenylfluorone color occured when this lead solution was poured into phenylfluorone. The presence of chlorine in hydrochloric acid solution bleaches phenylfluorone.

4. The phenylfluorone occasionally precipitated, even with the use of gum arabic, as Cluley suggests. An increase in gum arabic did not improve the solution. An increase in per cent of alcohol above the amount recommended by Cluley and occasional shaking during color development, were found necessary to give the best results.

5. The effect of Pb, Zn, and Cd on the development of the germanium-phenylfluorone color was tested and found to give no interference with germanium analysis.

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VITA

Franklin Maynard Hill was born in Brighton, Tennessee on January 4, 1919 where he finished high school in 1936. He received his B. A. degree from Erskine College, Due West, South Carolina in 1940. A veteran of World War II, he served as an officer in the Naval Reserve, most of the time on duty afloat in the South Pacific. Before coming to the Missouri School of Mines and Metallurgy he taught high school mathematics one year; worked as chief chemist for four years at Memphis Works, International Harvester; and for two years as chief chemist at Montana Ferroalloys in Memphis. He is married and has two children.